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ABSTRACT SUBMISSION FORM

Title of the Abstract: Stability and reproducibility of Ag colloidal pastes for Surface Enhanced Raman Spectroscopy (SERS) analysis of natural dyes in archaeological and historical textiles

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Stability and reproducibility of Ag colloidal pastes for Surface Enhanced Raman Spectroscopy (SERS) analysis of natural dyes in archaeological and historical textiles

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The detection and identification of natural dyes in ancient textiles is of central interest in cultural heritage studies to gain information on the historical context and on the manufacturing techniques, to elucidate trade routes in antiquity and even for the uncovering of forgeries.

Surface-Enhanced Raman Spectroscopy (SERS), using noble metal surfaces at the nanometre scale, represents an ideal analytical technique to detect dyes in artworks. Nanostructured noble metal substrates lead to enhanced Raman signals by a factor of up to 10 orders of magnitude, simultaneously reducing the amount of required sample and offering a highly specific molecular identification on an extremely small scale. Moreover, the use of these substrates largely quenches the interfering fluorescence generated by the dye.

Chemically reduced Ag colloids are among the most popular SERS substrates. Synthesis by chemical reducing agents has the advantage of being simple and presents a certain stability of the system, due to the adsorption of the reductant anions on the Ag surface, which confers a high electric charge to the suspended nanoparticles. Ag substrates produced according to Lee and Meisel [1] have been widely used. Several authors proposed modifications to this procedure suggesting the addition of chemical aggregating agents such as potassium nitrate [2], sodium chloride [3], sodium perchlorate [4] and sodium sulphate [5]. Conversely, the aggregation of the Ag nanoparticles may be achieved by concentrating the colloid through centrifugation and obtaining the so-called 'Ag colloidal pastes' [6, 7]

Among the different methodologies proposed to obtain SER spectra of dyes used in archaeological and historical objects, on-fibre SERS employing Ag pastes [7] can be very appropriate for valuable artefacts, because it strongly reduces the amount of required sample and does not need any extensive sample preparation.

On the other hand, SERS is extremely distance dependent, i.e.: the analysed molecule must be within the decay length of the electromagnetic fields to be detected. This can be challenging if we consider that it must replace the citrate surfactant surrounding the Ag nanoparticles and bind to the Ag surface. Moreover it is influenced by other factors, such as the morphology of the hot spots, the relative orientation of the molecule with respect to the SERS surface (which results in selective enhancement of certain peaks) and the difficulty in obtaining a completely reproducible aggregation of the Ag colloids. All these characteristics lead to an intrinsically variable response.

In the last few years, our activities in the field of SERS analysis of archaeological and historical dyes evidenced this variability both for different Ag paste batches synthesised at different times and for the same batch as a function of time. Thus, understanding the stability and reproducibility of the system would decisively improve the experimental planning and reduce the eventuality of discarding still active Ag paste.

Considering all these factors, the synthesis of different Ag paste batches was carried out to systematically evaluate: 1) the paste stability of different paste batches, by acquiring SER spectra on the same batch at different times (up to 10 weeks), 2) the reproducibility of the SERS response of the pastes within the same batch (*intra*-batch) and among different batches (*inter*-batch) at the same aging time, 3) the effect of a modification of the synthesis procedure (rapid cooling at the end of the chemical reduction thermal step) and 4) the

comparison of the spectroscopic response obtained on samples prepared with the same Ag paste at different aging times (NEW) with those on the same sample prepared with the newly synthesised paste and acquired at different times (SAME).

For each of the previous points the SERS responses of both Ag pastes (as signals of Ag and citrate are normally obtained) and a wool sample dyed with cochineal and used as a reference material were evaluated. For each sample 10-15 SERS spectra were acquired in order to highlight also the intrinsic variability of the system. Each spectrum was background-subtracted and the height of specific peaks (namely the peaks of Ag at about 230 cm^{-1} and citrate at about 930 cm^{-1} for the paste spectra and the peaks of Ag at about 230 cm^{-1} and carminic acid at about 1300 cm^{-1} for the reference material spectra, respectively) was measured.

One spectrum was selected from each measurement set. In particular, for the reference wool samples, the spectrum with the highest value of the intensity ratio of the carminic acid and Ag peaks (Coc/Ag) was considered.

The results evidenced that both on the Ag pastes and on the reference wool NEW samples, the aging effect is variable from one batch to another but the trend is towards a SERS efficiency increase with time until a maximum (which is observed at different aging times for different batches). The only exception is the Ag paste obtained with the alternative procedure, whose efficiency decreases constantly. As for the SERS measurements performed on the SAME samples, a different behaviour is observed for the pastes and for the reference wool. Indeed, the intensity of the spectra of the Ag pastes showed a constant decrease while the intensity ratio Coc/Ag generally increases, in some cases continuously up to 10 weeks and in other cases reaching a maximum value for intermediate aging times. Moreover, as far as the absolute intensities of the spectra are concerned, for the reference wool samples at each specific aging time Coc/Ag values are in most cases decisively higher for the samples prepared immediately after the paste synthesis and recorded at different aging times.

The overall results seem to suggest a substantial difficulty in obtaining systems characterised by a completely predictable behaviour in accordance to the inherent characteristics of the SERS technique.

On the other hand, the obtained data give precious indications on the optimal sample preparation procedure, indicating that the paste efficiency reaches a maximum after some time from the synthesis step and guaranteeing the possibility to analyse (and, eventually, re-analyse) the samples even after several weeks from the moment of their preparation.

Some of the obtained Ag pastes were then used for the analysis of dyes in various archaeological and historical textiles. The results obtained on these samples highlighted that, in addition to the characteristics of the Ag paste, the influence of the intrinsic characteristics of the material under investigation may play a role on the possibility of registering an informative SER spectrum.

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